

## DESCRIPTION

ELECTROLYTIC PROCESSING APPARATUS AND METHOD

## Technical Field

5 This invention relates to an electrolytic processing apparatus and method, and more particularly to an electrolytic processing apparatus and method useful for processing a conductive material present in the surface of a substrate, such as a semiconductor wafer, or for removing impurities adhering  
10 to the surface of a substrate.

## Background Art

In recent years, instead of using aluminum or aluminum alloys as a material for forming interconnection circuits on a substrate such as a semiconductor wafer, there is an eminent  
15 movement towards using copper (Cu) which has a low electric resistivity and high electromigration resistance. Copper interconnects are generally formed by filling copper into fine recesses formed in the surface of a substrate. There are known  
20 various techniques for forming such copper interconnects, including CVD, sputtering, and plating. According to any such technique, a copper film is formed in the substantially entire surface of a substrate, followed by removal of unnecessary copper by chemical mechanical polishing (CMP).

25 FIGS. 8A through 8C illustrate, in sequence of process steps, an example of forming such a substrate W having copper interconnects. As shown in FIG. 8A, an insulating film 2, such as an oxide film of SiO<sub>2</sub> or a film of low-k material, is deposited on a conductive layer 1a in which semiconductor devices are  
30 formed, which is formed on a semiconductor base 1. A contact hole 3 and a trench 4 for interconnects are formed in the insulating film 2 by the lithography/etching technique. Thereafter, a barrier layer 5 of TaN or the like is formed on

the entire surface, and a seed layer 7 as an electric supply layer for electroplating is formed on the barrier layer 5.

Then, as shown in FIG. 8B, copper plating is performed onto the surface of the substrate W to fill the contact hole 3 and the trench 4 with copper and, at the same time, deposit a copper film 6 on the insulating film 2. Thereafter, the copper film 6 and the barrier layer 5 on the insulating film 2 are removed by chemical mechanical polishing (CMP) so as to make the surface of the copper film 6 filled in the contact hole 3 and the trench 4 for interconnects and the surface of the insulating film 2 lie substantially on the same plane. An interconnection composed of the copper film 6 as shown in FIG. 8C is thus formed.

Components in various types of equipments have recently become finer and have required higher accuracy. As sub-micro manufacturing technology has commonly been used, the properties of materials are largely influenced by the processing method. Under these circumstances, in such a conventional machining method that a desired portion in a workpiece is physically destroyed and removed from the surface thereof by a tool, a large number of defects may be produced to deteriorate the properties of the workpiece. Therefore, it becomes important to perform processing without deteriorating the properties of the materials.

Some processing methods, such as chemical polishing, electrolytic processing, and electrolytic polishing, have been developed in order to solve this problem. In contrast with the conventional physical processing, these methods perform removal processing or the like through chemical dissolution reaction. Therefore, these methods do not suffer from defects, such as formation of an altered layer and dislocation, due to plastic deformation, so that processing can be performed without deteriorating the properties of the materials.

A processing method, which makes use of a catalytic

reaction of the ion exchanger and carries out processing in ultrapure water, has been developed as electrolytic processing. FIG. 9 illustrates the principle of this electrolytic processing. FIG. 9 shows the ionic state when an ion exchanger 12a mounted on a processing electrode 14 and an ion exchanger 12b mounted on a feeding electrode 16 are brought into contact with or close to a surface of a workpiece 10, while a voltage is applied via a power source 17 between the processing electrode 14 and the feeding electrode 16, and a liquid 18, e.g. ultrapure water, is supplied from a liquid supply section 19 between the processing electrode 14, the feeding electrode 16 and the workpiece 10. In the case of this electrolytic processing, water molecules 20 in the liquid 18 such as ultrapure water are dissociated efficiently by using the ion exchangers 12a, 12b into hydroxide ions 22 and hydrogen ions 24. The hydroxide ions 22 thus produced, for example, are carried, by the electric field between the workpiece 10 and the processing electrode 14 and by the flow of the liquid 18, to the surface of the workpiece 10 opposite to the processing electrode 14 whereby the density of the hydroxide ions 22 in the vicinity of the workpiece 10 is enhanced, and the hydroxide ions 22 are reacted with the atoms 10a of the workpiece 10. The reaction product 26 produced by this reaction is dissolved in the liquid 18, and removed from the workpiece 10 by the flow of the liquid 18 along the surface of the workpiece 10. Removal processing of the surface of the workpiece 10 is thus effected.

With the electrolytic processing of an electrically conductive material carried out by using an ion exchanger in the above-described manner, it is not possible to directly apply thereto a numerical control mechanism generally employed in conventional mechanical processing. In this regard, an electrolytic processing method utilizes a chemical interaction between  $\text{OH}^-$  ions and the atoms of a workpiece. Accordingly, the

processing phenomenon occurs even when a workpiece and a tool (electrode) is not in contact with each other. Electrolytic processing is thus differentiated in the processing principle from mechanical processing in which processing is effected by physical destruction of a workpiece. More specifically, in a common mechanical processing, processing is effected by allowing a workpiece and a tool, which are in contact with each other, to make a relative movement so as to physically destruct the workpiece. The progress of processing may be stopped by releasing the contact between the workpiece and the tool e.g. when a processing amount is reached to an intended processing amount. The processing does not progress any more even when the tool passes over the surface of the workpiece. On the other, according to the electrolytic processing method which utilizes a chemical interaction between the reaction species and a workpiece, as described above, the processing phenomenon occurs when the amount of the reaction species reaches a certain level, even when the tool (electrode) is not in contact with the workpiece. Accordingly, the processing phenomenon inevitably occurs when the tool (electrode) passes over the surface of a portion of the workpiece in which a predetermined amount of processing has been effected.

Accordingly, in order to perform processing of an electrically conductive material with a high processing precision that follows an intended form of a processed workpiece, by the electrolytic processing method utilizing the chemical interaction between the reaction species and the workpiece, such a control system is needed that does not simply control the contact state (position of tool) between the workpiece and the tool as is the case of mechanical processing, but also control the chemical interaction between the reaction species, such as  $\text{OH}^-$  ions, and the atoms of the workpiece.

### Disclosure of Invention

The present invention has been made in view of the above situation in the background art. It is therefore an object of the present invention to provide an electrolytic processing apparatus and method that can effect processing of a workpiece, having in the surface an electrically conductive material as a to-be-processed material, with high processing precision and can produce an intended form of processed workpiece with high accuracy of form.

In order to achieve the above object, the present invention provides an electrolytic processing apparatus, comprising: a holder for detachably holding a workpiece; a processing electrode that can come close to or into contact with the workpiece held by the holder; a feeding electrode for feeding electricity to the workpiece held by the holder; an ion exchanger disposed in at least one of the space between the workpiece and the processing electrode and the space between the workpiece and the feeding electrode; a fluid supply section for supplying a fluid between the workpiece and at least one of the processing electrode and the feeding electrode, in which the ion exchanger is present; a power source for applying a voltage between the processing electrode and the feeding electrode; a drive section for allowing the workpiece held by the holder and the processing electrode, facing each other, to make a relative movement; and a numerical controller for effecting a numerical control of the drive section.

The electrolytic processing apparatus makes it possible to compare the form of a workpiece before or during processing with an intended form of the workpiece after processing and determine the processing amount corresponding to the coordinate difference between the two forms, input parametric data corresponding to the processing amount to the numerical controller and, based on the inputted data, effect a numerical

control of the drive section that allows the workpiece held by the holder and the processing electrode, facing each other, to make a relative movement. The electrolytic processing apparatus, carried out under such a numerical control, can produce the intended form of processed workpiece with high accuracy of form.

The power source may supply an electric current or a voltage controlled at a constant value between the processing electrode and the feeding electrode.

In electrolytic processing, the processing rate is constant when the electric current flowing between a processing electrode and a feeding electrode is controlled at a constant value. In this case, the processing amount is determined by the product of the electric current value and the processing time. Accordingly, in the case where the electric current flowing between a processing electrode and a feeding electrode is controlled at a constant value, an intended form of processed workpiece can be obtained with high accuracy of form only by numerically controlling the processing time, i.e. a period of time during which the workpiece and the processing electrode face each other, so that the electrolytic processing phenomenon occurs (residence time).

The numerical controller may numerically control, for example, the relative movement speed between the workpiece held by the holder and the processing electrode via the drive section.

When carrying out electrolytic processing while allowing the workpiece held by the holder and the processing electrode, facing each other, to make a relative movement with changing relative speeds, the changing relative movement speeds may be numerically controlled. This makes it possible to process a certain point in the processing surface of the workpiece for an optimum processing time (residence time).

Alternatively, the numerical controller may numerically

control a stop time in a relative step movement of the workpiece held by the holder and the processing electrode via the drive section.

When carrying out electrolytic processing while allowing the workpiece held by the holder and the processing electrode, facing each other, to make a relative step movement, the stop time in the movement is numerically controlled. This makes it possible to process a certain point in the processing surface of the workpiece for an optimum processing time (residence time).

10 The term "relative step movement" herein refers to such a relative movement that either one or both of the workpiece and the processing electrode move so that the processing electrode makes a repetition of a certain-distance movement and stop over the workpiece.

15 The present invention provides an electrolytic processing method, comprising: providing a processing electrode, a feeding electrode and an ion exchanger disposed in at least one of the space between a workpiece held by a holder and the processing electrode and the space between the workpiece and the feeding electrode; allowing the processing electrode to be close to or in contact with the workpiece held by the holder while feeding electricity from the feeding electrode to the workpiece; supplying a fluid to the space between the workpiece and at least one of the processing electrode and the feeding electrode, in 20 which the ion exchanger is present; applying a voltage between the processing electrode and the feeding electrode; and allowing the workpiece held by the holder and the processing electrode, facing each other, to make a relative movement while numerically controlling the movement by a numerical controller.

30 The electrolytic processing method may be comprising: measuring the form of the workpiece before and/or during processing; inputting coordinate data on the measured form and on an intended form after processing of the workpiece to the

numerical controller; and numerically controlling the relative movement speed between the workpiece held by the holder and the processing electrode according to the coordinate difference between the measured form and the intended form.

5       The electrolytic processing method may be comprising: measuring the form of the workpiece before and/or during processing; inputting coordinate data on the measured form and on an intended form after processing of the workpiece to the numerical controller; and numerically controlling a stop time  
10 in a relative step movement of the workpiece held by the holder and the processing electrode according to the coordinate difference between the measured form and the intended form.

The above and other objects, features, and advantages of the present invention will be apparent from the following  
15 description when taken in conjunction with the accompanying drawings which illustrates preferred embodiments of the present invention by way of example.

#### **Brief Description of Drawings**

20       FIG. 1 is a longitudinal sectional front view of an electrolytic processing apparatus according to a first embodiment of the present invention;

FIG. 2 is a diagram illustrating the relationship between the pre-processing form and an intended post-processing form  
25 of a workpiece;

FIG. 3 is a block diagram illustrating an example of numerical control by the electrolytic processing apparatus of FIG. 1;

FIG. 4 is a longitudinal sectional front view of an  
30 electrolytic processing apparatus according to a second embodiment of the present invention;

FIG. 5 is a schematic perspective view of an electrolytic processing apparatus according to a third embodiment of the



present invention;

FIG. 6 is a block diagram illustrating an example of numerical control by the electrolytic processing apparatus of FIG. 5;

5        FIG. 7 is a schematic perspective view of an electrolytic processing apparatus according to a fourth embodiment of the present invention;

10        FIGS. 8A through 8C are diagrams illustrating, in sequence of process steps, an example of the formation of copper interconnects; and

FIG. 9 is a diagram illustrating the principle of electrolytic processing as carried out by using an ion exchanger.

#### **Best Mode for Carrying Out the Invention**

15        Preferred embodiments of the present invention will now be described with reference to the drawings. Though the below-described embodiments refer to application to electrolytic processing apparatuses (electrolytic polishing apparatuses) which use a substrate as a workpiece to be processed and remove (polish) copper formed on the surface of the substrate, the present invention is of course applicable to other workpiece, and to other electrolytic processing.

20        FIG. 1 shows an electrolytic processing apparatus according to a first embodiment of the present invention. This electrolytic processing apparatus includes a substrate holder 30 for attracting and holding the substrate W with its front surface facing upward (so-called "face-up" manner), and an electrode head 38 having a disc-shaped electrode section 36 made of an insulating material. The electrode section 36 has, 25 embedded therein, fan-shaped processing electrodes 32 and feeding electrodes 34 that are disposed alternately with their surfaces (lower faces) exposed. The electrode head 38 is 30 positioned above the substrate holder 30. An ion exchanger 40

consisting of laminated layers (lamination) is mounted on the lower surface of the electrode section 36 so as to cover the surfaces of the processing electrodes 32 and the feeding electrodes 34.

5       The substrate holder 30 is connected directly to the upper end of a supporting shaft 42 which is supported rotatably. A motor 44 as a first drive section for making the relative movement between the substrate W held by the substrate holder 30 and the processing electrodes 32 is disposed beside the supporting shaft  
10 42. A timing belt 46 is engaged between the supporting shaft 42 and the motor (first drive section) 44 so that the substrate holder 30 and the substrate W held by the substrate holder 30 rotate integrally by the actuation of the motor (first drive section) 44.

15       The electrode head 38 is connected downwardly to the free end of a pivot arm 48 which can pivot horizontally. The base portion of the pivot arm 48 is connected to the upper end of a hollow pivot shaft 54 which moves vertically via a ball screw 52 by the actuation of a motor 50 for vertical movement. A motor  
20 56, as a second drive section for making the relative movement between the substrate W held by the substrate holder 30 and the processing electrodes 32, is positioned beside the pivot shaft 54, and allows to move vertically with the pivot shaft 54. A timing belt 58 is engaged between the pivot shaft 54 and the  
25 motor (second drive section) 56 so that the pivot shaft 54 and the pivot arm 48 pivots (rotates) integrally by the actuation of the motor (second drive section) 56.

Further, the electrode head 38 is connected directly to a hollow motor 60 as a third drive section for making the relative  
30 movement between the substrate W held by the substrate holder 30 and the processing electrodes 32 so as to rotate by the actuation of the hollow motor (third drive section) 60.

In this embodiment, the ion exchanger 40 is of a

three-layer structure (lamination) consisting of a pair of strongly acidic cation-exchange fibers 62a, 62b and a strongly acidic cation-exchange membrane 62c interposed between the fibers 62a, 62b. The ion exchanger (laminate) 40 has a good water permeability and a high hardness and, in addition, the exposed surface (lower surface) to be opposed to the substrate W has a good smoothness. The construction of the ion exchanger 40 may be arranged such that the ion-exchange membrane is used for the exposed surface and the laminate of the ion-exchange fibers is arranged above the exposed ion-exchange membrane.

Each of the laminated layers 62a, 62b and 62c of the ion exchanger 40 preferably carries a strongly acidic cation-exchange group (sulfonic acid group), however, an ion exchanger carrying a weakly acidic cation-exchange group (carboxyl group), an ion exchanger carrying a strongly basic anion-exchange group (quaternary ammonium group), or an ion exchanger carrying a weakly basic anion-exchange group (tertiary or lower amino group) may be used.

The nonwoven fabric carrying a strongly basic anion-exchange group can be prepared by, for example, the following method: A polyolefin nonwoven fabric having a fiber diameter of 20-50  $\mu\text{m}$  and a porosity of about 90 % is subjected to the so-called radiation graft polymerization, comprising  $\gamma$ -ray irradiation onto the nonwoven fabric and the subsequent graft polymerization, thereby introducing graft chains; and the graft chains thus introduced are then aminated to introduce quaternary ammonium groups thereinto. The capacity of the ion-exchange groups introduced can be determined by the amount of the graft chains introduced. The graft polymerization may be conducted by the use of a monomer such as acrylic acid, styrene, glycidyl methacrylate, sodium styrenesulfonate or chloromethylstyrene. The amount of the graft chains can be controlled by adjusting the monomer concentration, the reaction temperature and the

reaction time. Thus, the degree of grafting, i.e. the ratio of the weight of the nonwoven fabric after graft polymerization to the weight of the nonwoven fabric before graft polymerization, can be made 500 % at its maximum. Consequently, the capacity of the ion-exchange groups introduced after graft polymerization can be made 5 meq/g at its maximum.

The nonwoven fabric carrying a strongly acidic cation-exchange group can be prepared by the following method: As in the case of the nonwoven fabric carrying a strongly basic anion-exchange group, a polyolefin nonwoven fabric having a fiber diameter of 20-50  $\mu$ m and a porosity of about 90 % is subjected to the so-called radiation graft polymerization comprising  $\gamma$ -ray irradiation onto the nonwoven fabric and the subsequent graft polymerization, thereby introducing graft chains; and the graft chains thus introduced are then treated with a heated sulfuric acid to introduce sulfonic acid groups thereinto. If the graft chains are treated with a heated phosphoric acid, phosphate groups can be introduced. The degree of grafting can reach 500 % at its maximum, and the capacity of the ion-exchange groups thus introduced after graft polymerization can reach 5 meq/g at its maximum.

The base material of each of the laminated layers 62a, 62b and 62c of the ion exchanger 40 may be a polyolefin such as polyethylene or polypropylene, or any other organic polymer. Further, besides the form of a nonwoven fabric, the ion exchanger may be in the form of a woven fabric, a sheet, a porous material, net or short fibers, etc.

When polyethylene or polypropylene is used as the base material, graft polymerization can be effected by first irradiating radioactive rays ( $\gamma$ -rays or electron beam) onto the base material (pre-irradiation) to thereby generate a radical, and then reacting the radical with a monomer, whereby uniform graft chains with few impurities can be obtained. When an

organic polymer other than polyolefin is used as the base material, on the other hand, radical polymerization can be effected by impregnating the base material with a monomer and irradiating radioactive rays ( $\gamma$ -rays, electron beam or UV-rays) onto the base material (simultaneous irradiation). Though this method fails to provide uniform graft chains, it is applicable to a wide variety of base materials.

By using each of the laminated layers 62a, 62b and 62c of the ion exchanger 40 made of a nonwoven fabric, which liquid can flows therethrough, having an anion-exchange group or a cation-exchange group, it becomes possible that the ion-exchange reaction between ions in the liquid and the ion-exchange group of the ion exchanger can be easily taken place.

When each of the laminated layers 62a, 62b and 62c of the ion exchanger 40 has only one of anion-exchange group and cation-exchange group, a limitation is imposed on electrolytically processible materials and, in addition, impurities are likely to form due to the polarity. In order to solve this problem, the anion exchangers and the cation exchangers may be superimposed, or each of the laminated layers 62a, 62b and 62c of the ion exchanger 40 may carry both of an anion-exchange group and a cation-exchange group per se, whereby a range of materials to be processed can be broadened and the formation of impurities can be restrained.

Further, by making the ion exchanger 40 a multi-layer structure consisting of laminated layers of ion-exchange materials, such as a nonwoven fabric, a woven fabric and a porous membrane, it is possible to increase the total ion exchange capacity of the ion exchanger 40, whereby formation of an oxide, for example, in removal (polishing) processing of copper, can be restrained to thereby avoid the oxide adversely affecting the processing rate. In this regard, when the total ion exchange capacity of an ion exchanger 40 is smaller than the amount of

copper ions taken in the ion exchanger 40 during removal processing, the oxide should inevitably be formed on the surface or in the inside of the ion exchanger 40, which adversely affects the processing rate. Thus, the formation of the oxide is governed by the ion exchange capacity of an ion exchanger, and copper ions exceeding the capacity should become the oxide. The formation of an oxide can thus be effectively restrained by using, as the ion exchanger, a multi-layer ion exchanger composed of laminated layers of ion-exchange materials which has enhanced total ion exchange capacity.

The ion exchanger 40 should preferably have water permeability and water-absorbing properties. Further, it is desirable that at least the material to be opposed to the workpiece has a high hardness and good surface smoothness. For example, a commercially-available foamed polyurethane "IC 1000" (manufactured by Rodel, Inc.), generally employed as a pad for CMP, is hard and excellent in wear resistance. By providing a number of through-holes, this product can be used as a material for each of the laminated layers of the ion exchanger 40. It is possible to provide holes in a resin plate, thereby making the plate water-permeable for use in the ion exchanger 40. It is of course desirable that the quality of the material has "water-absorbing properties".

According to this embodiment, a plurality of fan-shaped electrode plates 64 are disposed in the electrode section 36 in the circumference direction, and the cathode and anode of a power source 68 are alternately connected, via a slip ring 66, to the electrode plates 64. The electrode plates 64 connected to the cathode of the power source 68 become the processing electrodes 32 and the electrode plates 64 connected to the anode of the power source 68 become the feeding electrodes 34. This applies to processing of e.g. copper, because electrolytic processing of copper proceeds on the cathode side.

Depending upon a material to be processed, the cathode side can be a feeding electrode and the anode side can be a processing electrode. More specifically, when the material to be processed is copper, molybdenum, iron or the like, electrolytic processing proceeds on the cathode side, and therefore the electrode plates 64 connected to the cathode of the power source 68 should be the processing electrodes 32 and the electrode plates 64 connected to the anode should be the feeding electrodes 34. In the case of aluminum, silicon or the like, on the other hand, electrolytic processing proceeds on the anode side. Accordingly, the electrode plates connected to the anode of the power source should be the processing electrodes and the electrode plates connected to the cathode should be the feeding electrodes.

By thus disposing the processing electrodes 32 and the feeding electrodes 34 separately and alternately in the circumferential direction of the electrode section 36, fixed feeding portions to supply electricity to a conductive film (portion to be processed) of the substrate is not needed, and processing can be effected to the entire surface of the substrate. Further, by changing the positive and negative in a pulse manner or alternately, an electrolysis product can be dissolved and the flatness of the processed surface can be enhanced by the multiplex repetition of processing.

With respect to the processing electrode 32 and the feeding electrode 34, oxidation or dissolution thereof due to an electrolytic reaction is generally a problem. In view of this, it is preferred to use, as a base material of the feeding electrode 34, carbon, a noble metal that is relatively inactive, a conductive oxide or a conductive ceramics, rather than a metal or metal compound widely used for electrodes. A noble metal-based electrode may, for example, be one obtained by plating or coating platinum or iridium onto a titanium electrode,

and then sintering the coated electrode at a high temperature to stabilize and strengthen the electrode. Ceramics products are generally obtained by heat-treating inorganic raw materials, and ceramics products having various properties are produced from various raw materials including oxides, carbides and nitrides of metals and nonmetals. Among them there are ceramics having an electric conductivity. When an electrode is oxidized, the value of the electric resistance generally increases to cause an increase of applied voltage. However, by protecting the surface of an electrode with a non-oxidative material such as platinum or with a conductive oxide such as an iridium oxide, the decrease of electric conductivity due to oxidation of the base material of an electrode can be prevented.

A pure water nozzle 70 as a pure water supply section for supplying pure water or ultrapure water toward the space between the substrate W held by the substrate holder 30 and the lowered electrode head 38 is disposed above the substrate holder 30. Pure water or ultrapure water is thus supplied to the ion exchanger 40. Pure water herein refers to a water having an electric conductivity of not more than  $10 \mu\text{S/cm}$ , and ultrapure water refers to a water having an electric conductivity of not more than  $0.1 \mu\text{S/cm}$ . The electric conductivity of the present invention refers herein to that at  $25^\circ\text{C}$ , 1atm. Instead of pure water or ultrapure water, a liquid having an electric conductivity of not more than  $500 \mu\text{S/cm}$  or any electrolytic solution may be used. By supplying such a liquid during processing, the instability factors of processing, such as process products and dissolved gases, can be removed, and processing can be effected uniformly with good reproducibility.

The electrolytic processing apparatus is provided with a numerical controller 72 for effecting numerical control of the drive sections, i.e. the motor (first drive section) 44, the motor (second drive section) 56 and the motor (third drive



section) 60, which allow the substrate W held by the substrate holder 30 and the processing electrodes 32, facing each other, to make a relative movement. The motors (drive sections) 44, 56 and 60 are thus numerically controllable servomotors, and  
5 their rotation angles and rotational speeds are numerically controlled by an output signal from the numerical controller 72.

According to this embodiment, during electrolytic processing carried out while being flowed an electric current  
10 at a constant value between the processing electrodes 32 and the feeding electrodes 34, the numeral controller 72 numerically controls: the rotational speed of the substrate W, held by the substrate holder 30, via the motor (first drive section) 44; the speed of the horizontal movement of the electrode head 38,  
15 by pivoting of the pivot arm 48, via the motor (second drive section) 56; and the rotational speed of the electrode head 38 via the motor (third drive section) 60.

An example of the numerical control will now be described with reference to FIGS. 2 and 3. First, as shown in FIG. 2, the  
20 form of a substrate (workpiece) before processing is measured. Specifically, various coordinate points of the pre-processing form are measured in a X-Y-Z coordinate system (in which the Z axis is orthogonal to the X-Y plane as a datum plane). The measured pre-processing form data is inputted to the numerical  
25 controller 72. Further, with respect to a coordinate point (x, y, Z<sub>1</sub>) of the pre-processing form, the corresponding coordinate point (x, y, Z<sub>2</sub>) of an intended post-processing form is also inputted as intended form data to the numerical controller 72. In addition, unit processing form data (movement speed per motor  
30 control signal pulse) e.g. on form and on processing rate is inputted to the numerical controller 72 in advance or at an arbitrary time.

When electrolytic processing is carried out under control

of the electric current flowing between the processing electrodes 32 and the feeding electrodes 34 at a constant value, the processing rate is constant thereby the processing amount is determined by the product of the current value and the processing time. Accordingly, in the case where the electric current flowing between the processing electrodes 32 and the feeding electrodes 34 is controlled at a constant value, an intended form of processed substrate can be obtained with high accuracy of form only by numerically controlling the processing time, i.e. a period of time during which the substrate W and the processing electrodes 32 face each other, so that the electrolytic processing phenomenon occurs (residence time).

Thus, according to this embodiment, a processing amount  $Z_1$ - $Z_2$  in the Z direction is determined at each coordinate point based on the data inputted in the numerical controller 72. Based on the processing amount  $Z_1$ - $Z_2$ , the rotational speed of the substrate W, held by the substrate holder 30, via the motor (first drive section) 44; the speed of the horizontal movement of the electrode head 38, by pivoting of the pivot arm 48, via the motor (second drive section) 56; and the rotational speed of the electrode head 38 via the motor (third drive section) 60 are determined for each coordinate point, and the signal is inputted to the motors (drive sections) 44, 56 and 60 so as to numerically control the motors (drive sections) 44, 56 and 60.

Next, electrolytic processing by this electrolytic processing apparatus will be described.

First, a substrate W, e.g. a substrate W as shown in FIG. 8B which has in its surface a copper film 6 as a conductor film (portion to be processed), is attracted and held by the substrate holder 30, and the electrode head 38 is moved by the pivot arm 48 to a processing position right above the substrate W held by the substrate holder 30. The electrode head 38 is then lowered by the actuation of the motor 50 for vertical movement, so that

the ion exchanger 40 mounted on the lower surface of the electrode section 36 of the electrode head 38 contacts or gets close to the upper surface of the substrate W held by the substrate holder 30.

5       Next, an electric power is applied from the power source 68 to between the processing electrodes 32 and the feeding electrodes 34, while the electric current flowing between the processing electrodes 32 and the feeding electrodes 34 being controlled at a constant value, and the substrate holder 30 and  
10       the electrode head 38 are rotated. Further, the pivot arm 48 is pivoted to move the electrode head 38 horizontally. At the same time, pure water or ultrapure water is supplied from the pure water nozzle 70 disposed above the electrode substrate holder 30 to between the substrate W and the electrode head 38,  
15       thereby filling pure water or ultrapure water into the space between the processing and feeding electrodes 32, 34 and the substrate W. Thereby, electrolytic processing of the conductor film (copper film 6) formed on the substrate W is effected by hydrogen ions or hydroxide ions produced in the ion exchanger  
20       40.

More specifically, pure water or ultrapure water is dissociated into  $\text{OH}^-$  ions and  $\text{H}^+$  ions with the aid of a catalytic reaction in the ion exchanger 40. The  $\text{OH}^-$  ions transfer the electric charges in the vicinity of the processing electrodes  
25       32 and become OH radicals. The OH radicals are reacted with the copper film 6 of the substrate W to thereby effect removal (polishing) processing of the copper film 6. In order to shut off  $\text{H}_2$  gas generated at the feeding electrodes 34, a gas-impermeable ion membrane may be used as the strongly acidic  
30       cation-exchange membrane 62. The  $\text{H}_2$  gas is thus shut off, and is discharged out by the flow of pure water or ultrapure water produced by the rotation of the electrode section 36.

More specifically, by allowing pure water or ultrapure

water to flow within the ion exchanger 40, a sufficient amount of water can be supplied to a functional group (sulfonic acid group in the case of an ion exchanger carrying a strongly acidic cation-exchange group) thereby to increase the amount of dissociated water molecules, and the process product (including a gas) formed by the reaction between the conductor film (copper film 6) and hydroxide ions (or OH radicals) can be removed by the flow of water, whereby the processing efficiency can be enhanced. The flow of pure water or ultrapure water is thus necessary, and the flow of water should desirably be constant and uniform. The constancy and uniformity of the flow of water leads to constancy and uniformity in the supply of ions and the removal of the process product, which in turn leads to constancy and uniformity in the processing.

By making the ion exchanger 40 of a laminate of a multi-layer structure, the total ion-exchange capacity of the ion exchanger (laminate) 40 can be increased, whereby the reaction products (oxides and ions) of the electrolytic reaction can be prevented from accumulating in the ion exchanger 40 in an amount exceeding the accumulation capacity of the laminate. In this regard, if the reaction products are accumulated in the laminate in an amount exceeding the accumulation capacity, the accumulated products may change their forms, and such transformed products can adversely affect the processing rate and its distribution. Moreover, the flatness of the processed surface of the substrate can be enhanced by using, as the ion exchanger 40, one having a high hardness or one having a good surface smoothing, or by using both of them.

In advance, the pre-processing form data, intended form data and the unit processing form data are inputted to the numerical controller 72. Electrolytic processing is carried out while numerically controlling: the rotational speed of the substrate W, held by the substrate holder 30, via the motor (first

drive section) 44; the speed of the horizontal movement of the electrode head 38, by pivoting of the pivot arm 48, via the motor (second drive section) 56; and the rotational speed of the electrode head 38 via the motor (third drive section) 60.

5 In the electrolytic processing, the electric current flowing between the processing electrodes 32 and the feeding electrodes 34 is controlled at a constant value to thereby fix the processing rate while the relative movement between the substrate W and the processing electrodes 32 being numerically  
10 controlled. The electrolytic processing can produce an intended form of processed substrate (workpiece) W with high accuracy of form.

After completion of the electrolytic processing, the power source 68 is disconnected, the rotation of the substrate holder  
15 30 and the electrode head 38 are stopped, and pivoting of the pivot arm 48 is stopped. Thereafter, the electrode head 38 is raised, and processed substrate W held by the substrate holder 30 is transferred to next process.

This embodiment shows the case of supplying pure water,  
20 preferably ultrapure water, to the space between the electrode section 36 and the substrate W. The use of pure water or ultrapure water containing no electrolyte upon electrolytic processing can prevent extra impurities such as an electrolyte from adhering to and remaining on the surface of the substrate  
25 W. Further, copper ions or the like dissolved during electrolytic processing are immediately caught by the ion exchanger 40 through the ion-exchange reaction. This can prevent the dissolved copper ions or the like from re-precipitating on the other portions of the substrate W, or from  
30 being oxidized to become fine particles which contaminate the surface of the substrate W.

Ultrapure water has a high resistivity, and therefore an electric current is hard to flow therethrough. A lowering of

the electric resistance is made by shortening a distance between the electrode and the workpiece, or interposing the ion exchanger between the electrode and the workpiece. Further, an electrolytic solution, when used in combination with  
5 electrolytic solutions, can further lower the electric resistance and reduce the power consumption. When electrolytic processing is conducted by using an electrolytic solution, the portion of a workpiece that undergoes processing ranges over a slightly wider area than the area of the processing electrode.

10 In the case of the combined use of ultrapure water and the ion exchanger, on the other hand, since almost no electric current flows through ultrapure water, electric processing is effected only within the area of a workpiece that is equal to the area of the processing electrode and the ion exchanger.

15 It is possible to use, instead of pure water or ultrapure water, an electrolytic solution obtained by adding an electrolyte to pure water or ultrapure water. The use of such an electrolytic solution can further lower the electric resistance and reduce the power consumption. A solution of a  
20 neutral salt such as NaCl or Na<sub>2</sub>SO<sub>4</sub>, a solution of an acid such as HCl or H<sub>2</sub>SO<sub>4</sub>, or a solution of an alkali such as ammonia, may be used as the electrolytic solution, and these solutions may be selectively used according to the properties of the workpiece. When the electrolytic solution is used, it is preferred to  
25 provide a slight interspace between the substrate W and the ion exchanger 40 so that they are not in contact with each other.

Further, it is also possible to use, instead of pure water or ultrapure water, a liquid obtained by adding a surfactant or the like to pure water or ultrapure water, and having an  
30 electric conductivity of not more than 500  $\mu$ S/cm, preferably not more than 50  $\mu$ S/cm, more preferably not more than 0.1  $\mu$ S/cm (resistivity of not less than 10 M $\Omega$ ·cm). Due to the presence of a surfactant in pure water or ultrapure water, the liquid

can form a layer, which functions to inhibit ion migration evenly, at the interface between the substrate W and the ion exchanger 40, thereby moderating concentration of ion exchange (metal dissolution) to enhance the flatness of the processed surface.

5 The surfactant concentration is desirably not more than 100 ppm. When the value of the electric conductivity is too high, the current efficiency is lowered and the processing rate is decreased. The use of the liquid having an electric conductivity of not more than 500  $\mu\text{S/cm}$ , preferably not more  
10 than 50  $\mu\text{S/cm}$ , more preferably not more than 0.1  $\mu\text{S/cm}$ , can attain a desired processing rate.

According to the embodiment, the processing rate can be considerably enhanced by interposing the ion exchanger 40 between the substrate W and the processing and feeding electrodes  
15 32, 34. In this regard, electrochemical processing using ultrapure water is effected by a chemical interaction between hydroxide ions in ultrapure water and a material to be processed. However, the amount of the hydroxide ions acting as reactant in ultrapure water is as small as  $10^{-7}$  mol/L under normal  
20 temperature and pressure conditions, so that the removal processing efficiency can decrease due to reactions (such as an oxide film-forming reaction) other than the reaction for removal processing. It is therefore necessary to increase hydroxide ions in order to conduct removal processing  
25 efficiently. A method for increasing hydroxide ions is to promote the dissociation reaction of ultrapure water by using a catalytic material, and an ion exchanger can be effectively used as such a catalytic material. More specifically, the activation energy relating to water-molecule dissociation  
30 reaction is lowered by the interaction between functional groups in an ion exchanger and water molecules, whereby the dissociation of water is promoted to thereby enhance the processing rate.

Further, according to this embodiment, the ion exchanger

40 is brought into contact with or close to the substrate W upon electrolytic processing. When the ion exchanger 40 is positioned close to the substrate W, though depending on the distance therebetween, the electric resistance is large to some degree and, therefore, a somewhat large voltage is necessary to provide a requisite electric current density. However, on the other hand, because of the non-contact relation, it is easy to form flow of pure water or ultrapure water along the surface of the substrate W, whereby the reaction product produced on the substrate surface can be efficiently removed. In the case where the ion exchanger 40 is brought into contact with the substrate W, the electric resistance becomes very small and therefore only a small voltage needs to be applied, whereby the power consumption can be reduced.

If a voltage is raised to increase the current density in order to enhance the processing rate, an electric discharge can occur when the electric resistance between the electrode and the substrate (workpiece to be processed) is large. The occurrence of electric discharge causes etch pits on the surface of the workpiece, thus failing to form an even and flat processed surface. To the contrary, since the electric resistance is very small when the ion exchanger 40 is in contact with the substrate W, the occurrence of an electric discharge can be avoided.

FIG. 4 shows an electrolytic processing apparatus according to a second embodiment of the present invention. The electrolytic processing apparatus has a ring-shaped contact holding plate 80 at the periphery of the upper surface of the substrate holder 30. A plurality of inwardly-protruding contacts 82 as feeding electrodes are mounted at a given pitch to the contact holding plate 80. Further, the electrode head 38 is provided with a processing electrode 84 instead of the electrode section 36 used in the embodiment of FIG. 1. The processing electrode 84 is connected to the cathode of the power



source 68 via a slip ring 86, and the contacts (feeding electrodes) 82 are connected to the anode of the power source 68. The other construction is the same as the apparatus shown in FIG. 1.

5        According to this embodiment, when a substrate W is held by the substrate holder 30, the contacts (feeding electrodes) 82 contact the copper layer 6 as a to-be-processed material, deposited on the surface of the substrate W as shown in FIG. 8B. Electrolytic processing can be carried in the same manner  
10 as in the preceding embodiment. Thus, the electrode head 38 is lowered, and a electric current is applied from the power source 68 to between the processing electrode 84 and the contacts (feeding electrodes) 82 at a constant value while the substrate holder 30 and the electrode head 38 being rotated, and the pivot  
15 arm 48 being pivoted to move the electrode head 38 horizontally. At the same time, pure water or ultrapure water is supplied from the pure water nozzle 70 to between the substrate W and the processing electrode 84. Electrolytic processing of the conductive film (copper film 6) of the substrate W is thus  
20 effected.

      In advance of the electrolytic processing, as with the processing embodiment described above, the pre-processing form data, the intended form data, the unit processing form data are inputted to the numerical controller 72 so as to numerically  
25 control: the rotational speed of the substrate W, held by the substrate holder 30, via the motor (first drive section) 44; the speed of the horizontal movement of the electrode head 38, by pivoting of the pivot arm 48, via the motor (second drive section) 56; and the rotational speed of the electrode head 38  
30 via the motor (third drive section) 60. The electrolytic processing carried out under such a control can produce an intended form of processed substrate W with high accuracy of form.

FIG. 5 shows an electrolytic processing apparatus according to a third embodiment of the present invention. The electrolytic processing apparatus includes a substrate holder 100 for attracting and holding a substrate W with its front surface facing upward, and a columnar or cylindrical processing electrode 102 disposed above the substrate holder 100. The processing electrode 102 is coupled to the free end of a horizontally-extending rotating shaft 104 that is rotatable and vertically movable. An ion exchanger 106 is mounted tightly on the outer circumferential surface of the processing electrode 102. The substrate holder 100 and the processing electrode 102 are disposed in a processing bath (not shown) filled with a fluid, such as ultrapure water or pure water, that is, they are immersed in the fluid.

The substrate holder 100 is coupled to the upper surface of a rotating body 108 that rotates about a Z axis in the direction of  $\theta$ . The rotating body 108 is mounted on the upper surface of an X-Y table 118 which includes an X stage 112 that moves in the X direction by the actuation of a motor 110 as a first drive section for allowing the substrate W, held by the substrate holder 100, and the processing electrode 102 to make a relative movement in the X direction, and a Y stage 116 that moves in the Y direction by the actuation of a motor 114 as a second drive section for allowing the substrate W, held by the substrate holder 100, and the processing electrode 102 to make a relative movement in the Y direction.

A wire extending from the cathode of a power source 120 is connected to the processing electrode 102, and a wire extending from the anode is connected to a feeding electrode 122 that is connected to an electric conductor, e.g. copper film 6 formed in the substrate W as shown in FIG. 8B, and feeds electricity to the conductor.

The processing bath is provided with a fluid nozzle as a

fluid supply section for supplying a fluid, such as pure water or ultrapure water, into the processing bath.

The electrolytic processing apparatus is provided with a numerical controller 124 for effecting a numerical control of the drive sections, i.e. the motor 110 (first drive section) and the motor 114 (second drive section), which allow the substrate W, held by the substrate holder 100, and the processing electrode 102, facing each other, to make a relative movement. The motors (drive sections) 110, 114 are thus numerically controllable servomotors, and their rotation angles and rotational speeds are numerically controlled by an output signal from the numerical controller 124.

An example of the numerical control will now be described with reference to FIG. 6. First, as illustrated in FIG. 2, the form of the substrate (workpiece) before processing is measured by measuring various coordinate points of the pre-processing form in an X-Y-Z coordinate system (in which the Z axis is orthogonal to the X-Y plane as a datum plane). The measured pre-processing form data is inputted to the numerical controller 124. Further, with respect to a coordinate point (x, y,  $Z_1$ ) of the pre-processing form, the corresponding coordinate point (x, y,  $Z_2$ ) of an intended post-processing form is also inputted to the numerical controller 124. In addition, unit processing form data (movement speed per motor control signal pulse) e.g. on form and on processing rate is inputted to the numerical controller 124 in advance or at an arbitrary time.

According to this embodiment, a processing amount  $Z_1-Z_2$  in the Z direction is determined at each coordinate point based on the data inputted in the numerical controller 124. Based on the processing amount  $Z_1-Z_2$ , a period of time during which the substrate W held by the substrate holder 100 is stopped via the motor (first drive section) 110 and the motor (second drive section) 114, is determined, and the signal is inputted to the

motors (drive sections) 110, 114 so as to numerically control the motors 110, 114.

According to this embodiment, e.g. a substrate W as shown in FIG. 8B, having copper film 6 as a conductive film (to-be-processed portion) in the surface, is attracted and held by the substrate holder 100. The ion exchanger 106 mounted on the surface of the processing electrode 102 is brought close to or into contact with the surface (upper surface) of the substrate W. Electrolytic processing is then carried out by supplying an electric current from the power source 120 to between the processing electrode 102 and the feeding electrode 122 at a constant value while rotating the processing electrode 102.

During the electrolytic processing, a step movement, i.e. a repetition of a movement and stop of the substrate W in the X or Y direction, is carried out by the X-Y table 118. For this operation, as described above, the pre-processing form data, the intended form data and the unit processing form data are inputted to the numerical controller 124 in advance, thereby numerically controlling the stop time of the substrate W held by the substrate holder 100 via the motor (first drive section) 110 and the motor (second drive section) 114. The electrolytic processing performed with such a controlled relative step movement can produce the intended form of processed substrate with high accuracy of form.

The term "relative step movement" herein refers to such a relative movement that either one or both of the substrate W and the processing electrode 102 move so that the processing electrode 102 makes a repetition of a certain distance-movement and stop over the substrate W.

FIG. 7 shows an electrolytic processing apparatus according to a fourth embodiment of the present invention. This embodiment differs from the third embodiment shown in FIG. 5 in the use of a spherical or oval processing electrode 102a.

When the processing electrode 102a is lowered, an ion exchanger 106a, which is mounted on the surface of the processing electrode 102a, is brought into point contact with the substrate W. The processing electrode 102a is allowed to rotate while the ion  
5 exchanger is in such contact with the substrate W. The other construction is the same as the third embodiment.

According to this embodiment, the area of a portion (point) under processing is small, whereby supply of ultrapure water or pure water to around the processing portion can be made with  
10 ease, enabling a stable processing.

According to the above-described embodiments, the drive sections, which allow the substrate held by the substrate holder and the processing electrode to make a relative movement, are numerically controlled while the electric current flowing  
15 between the processing electrode and the feeding electrode is controlled at a constant value. It is, however, also possible to control the voltage applied between the processing electrode and the feeding electrode at a constant value, determine the electric current flowing between the processing electrode and  
20 the feeding electrode from the relationship between the voltage and electric current, and numerically control the drive sections based on the electric current thus determined.

The measurement of the form of a substrate (workpiece) may be carried out not only before processing but also at any time  
25 during processing any number of times. In this connection, there is a case where the actual processing time becomes different from a predetermined processing time. The difference can lead to a lowered accuracy of form of the resulting processed substrate. Such a lowering of accuracy may be eliminated or  
30 reduced by effecting in-processing measurement of the substrate as many times as possible. Thus, an increased number of in-processing measurements can generally enhance the processing precision.

As described hereinabove, the present invention makes it possible to compare the form of a workpiece before or during processing with an intended form of the workpiece after processing and determine the processing amount corresponding to the coordinate difference between the two forms, input parametric data corresponding to the processing amount to the numerical controller and, based on the inputted data, effect numerical control of the drive section that allows the workpiece held by the holder and the processing electrode, facing each other, to make a relative movement. The electrolytic processing, carried out under such a numerical control, can produce the intended form of processed workpiece with high accuracy of form.

Although certain preferred embodiments of the present invention have been shown and described in detail, it should be understood that various changes and modifications may be made therein without departing from the scope of the appended claims.

#### **Industrial Applicability**

This invention relates to an electrolytic processing apparatus and method useful for processing a conductive material present in the surface of a substrate, such as a semiconductor wafer, or for removing impurities adhering to the surface of a substrate.